

5           COMPOUNDS CONTAINING QUATERNARY CARBONS AND  
SILICON-CONTAINING GROUPS, MEDICAL DEVICES, AND  
METHODS

Cross Reference to Related Applications

This application claims priority to U.S. Provisional Application No. 10 60/411,725, filed on September 17, 2002, and U.S. Provisional Application No. 60/490,780, filed on July 29, 2003, which are incorporated herein by reference in their entireties.

Field of the Invention

15         This invention relates to compounds containing quaternary carbons and silicon-containing groups, preferably such compounds are polymers containing urethane and/or urea groups, particularly elastomers. Such materials are particularly useful as biomaterials in medical devices.

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Background of the Invention

The chemistry of polyurethanes and/or polyureas is extensive and well developed. Typically, polyurethanes and/or polyureas are made by a process in which a polyisocyanate is reacted with a molecule having at least two functional groups reactive with the polyisocyanate, such as a polyol or polyamine. The resulting polymer can be further reacted with a chain extender, such as a diol or diamine, for example. The polyol or polyamine is typically a polyester, polyether, or polycarbonate polyol or polyamine, for example.

30         Polyurethanes and/or polyureas can be tailored to produce a range of products from soft and flexible to hard and rigid. They can be extruded, injection molded, compression molded, and solution spun, for example. Thus, polyurethanes and polyureas, particularly



polyurethanes, are important biomedical polymers, and are used in implantable devices such as artificial hearts, cardiovascular catheters, pacemaker lead insulation, etc.

- Commercially available polyurethanes used for implantable
- 5 applications include BIOSPAN segmented polyurethanes, manufactured by Polymer Technology Group of Berkeley, CA, PELLETHANE segmented polyurethanes, sold by Dow Chemical, Midland, MI, and TECOFLEX segmented polyurethanes sold by Thermedics Polymer Products, Wilmington, MA. Polyurethanes are described in the article
- 10 "Biomedical Uses of Polyurethanes," by Coury et al., in *Advances in Urethane Science and Technology*, 9, 130-168, edited by Kurt C. Frisch and Daniel Klempner, Technomic Publishing Co., Lancaster, PA (1984). Typically, polyether polyurethanes exhibit more biostability than polyester polyurethanes and polycarbonate polyurethanes, as these are
- 15 more susceptible to hydrolysis. Thus, polyether polyurethanes are generally preferred biopolymers.

Polyether polyurethane elastomers, such as PELLETHANE 2363-80A (P80A) and 2363-55D (P55D), which are prepared from polytetramethylene ether glycol (PTMEG) and methylene

20 bis(diisocyanatobenzene) (MDI) extended with 1,4-butanediol (BDO), are widely used for implantable cardiac pacing leads. Pacing leads are electrodes that carry stimuli to tissues and biologic signals back to implanted pulse generators. The use of polyether polyurethane elastomers as insulation on such leads has provided significant

25 advantage over silicone rubber, primarily because of the higher tensile strength of the polyurethanes.

There is some problem, however, with biodegradation of polyether polyurethane insulation, which can cause failure. Polyether polyurethanes are susceptible to oxidation in the body, particularly in

30 areas that are under stress. When oxidized, polyether polyurethane elastomers can lose strength and can form cracks, which might eventually breach the insulation. This, thereby, can allow bodily fluids to enter the lead and form a short between the lead wire and the

implantable pulse generator (IPG). It is believed that the ether linkages degrade, perhaps due to metal ion catalyzed oxidative attack at stress points in the material.

One approach to solving this problem has been to coat the  
5 conductive wire of the lead. Another approach has been to add an antioxidant to the polyurethane. Yet another approach has been to develop new polyurethanes that are more resistant to oxidative attack. Such polyurethanes include only segments that are resistant to metal induced oxidation, such as hydrocarbon- and carbonate-containing  
10 segments. For example, polyurethanes that are substantially free of ether and ester linkages have been developed. This includes the segmented aliphatic polyurethanes of U.S. Pat. No. 4,873,308 (Coury et al.). Another approach has been to include a sacrificial moiety (preferably in the polymer backbone) that preferentially oxidizes relative  
15 to all other moieties in the polymer, which upon oxidation provides increased tensile strength relative to the polymer prior to oxidation. This is disclosed in U.S. Pat. Nos. 5,986,034 (DiDomenico et al.), 6,111,052 (DiDomenico et al.), and 6,149,678 (DiDomenico et al.).

Although such materials produce more stable implantable devices  
20 than polyether polyurethanes, there is still a need for biostable polymers, particularly polyurethanes suitable for use as insulation on pacing leads.

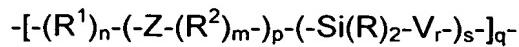
### Summary of the Invention

The present invention relates to compounds, preferably polymers,  
25 that include diorgano groups having quaternary carbons and silicon-containing groups. The silicon-containing groups are typically silane- and/or siloxane-containing groups. Particularly preferred polymers include urethane groups, urea groups, or combinations thereof (i.e., polyurethanes, polyureas, or polyurethane-ureas). Polymers of the  
30 present invention may be random, alternating, block, star block, segmented, or combinations thereof. Preferably, the polymer is a segmented polyurethane. Such polymers are preferably used as

biomaterials in medical devices. Preferred polymers are also preferably substantially free of ester, ether, and carbonate linkages.

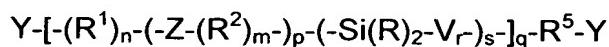
The present invention provides a polymer, and a medical device incorporating such polymer, which includes a group of the formula:

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wherein: n = 0 or 1; m = 0 or 1; p = 1-100,000; r = 0-100,000; s = 1-100,000; q = 1-100,000; R<sup>1</sup> and R<sup>2</sup> are each independently a saturated or unsaturated aliphatic group, an aromatic group, or combinations thereof, optionally including heteroatoms (preferably the aromatic groups are within the backbone); Z is -C(R<sup>3</sup>)<sub>2</sub>- wherein each R<sup>3</sup> is independently (i.e., may be the same or different) a saturated or unsaturated aliphatic group, an aromatic group, or combinations thereof, optionally including heteroatoms, wherein the two R<sup>3</sup> groups within -C(R<sup>3</sup>)<sub>2</sub>- can be optionally joined to form a ring; each R is independently a saturated or unsaturated aliphatic group, an aromatic group, or combinations thereof, optionally including heteroatoms; and V is -O-Si(R)<sub>2</sub>- or R<sup>1</sup>.

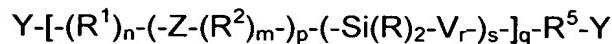
The present invention also provides a polymer, and a medical device that incorporates such polymer, wherein the polymer is prepared from a polymeric starting compound of the formula:



wherein: each Y is independently OH or NR<sup>4</sup>H; n = 0 or 1; m = 0 or 1; p = 1-100,000; r = 0-100,000; s = 1-100,000; q = 1-100,000; R<sup>1</sup>, R<sup>2</sup>, and R<sup>5</sup> are each independently a saturated or unsaturated aliphatic group, an aromatic group, or combinations thereof, optionally including heteroatoms (preferably, the aromatic groups are within the backbone); Z is -C(R<sup>3</sup>)<sub>2</sub>- wherein each R<sup>3</sup> is independently a saturated or unsaturated aliphatic group, an aromatic group, or combinations thereof, optionally including heteroatoms, wherein the two R<sup>3</sup> groups within -C(R<sup>3</sup>)<sub>2</sub>- can be optionally joined to form a ring; each R is independently

a saturated or unsaturated aliphatic group, an aromatic group, or combinations thereof, optionally including heteroatoms; each R<sup>4</sup> is independently H or a saturated or unsaturated aliphatic group, an aromatic group, or combinations thereof; V is -O-Si(R)<sub>2</sub>- or R<sup>1</sup>.

- 5       Also provided is a compound (starting material) of the formula:



- wherein: each Y is independently OH or NR<sup>4</sup>H; n = 0 or 1; m = 0 or 1;  
10 p = 1-100,000; r = 0-100,000; s = 1-100,000; q = 1-100,000; R<sup>1</sup>, R<sup>2</sup>, and R<sup>5</sup> are each independently a saturated or unsaturated aliphatic group, an aromatic group, or combinations thereof, optionally including heteroatoms (preferably, the aromatic groups are within the backbone); Z is -C(R<sup>3</sup>)<sub>2</sub>- wherein each R<sup>3</sup> is independently a saturated or  
15 unsaturated aliphatic group, an aromatic group, or combinations thereof, optionally including heteroatoms, wherein the two R<sup>3</sup> groups within -C(R<sup>3</sup>)<sub>2</sub>- can be optionally joined to form a ring; each R is independently a saturated or unsaturated aliphatic group, an aromatic group, or combinations thereof, optionally including heteroatoms; each R<sup>4</sup> is  
20 independently H or a saturated or unsaturated aliphatic group, an aromatic group, or combinations thereof; and V is -O-Si(R)<sub>2</sub>- or R<sup>1</sup>.

It should be understood that in the above formulas, each of the units (e.g., R<sup>1</sup>, -Z-(R<sup>2</sup>)<sub>m</sub>, -(-Si(R)<sub>2</sub>-V<sub>r</sub>)<sub>s</sub>, and V) (if repeated) can vary within any one molecule.

- 25       As written, the formulas provided herein (for both the resultant polymers and the polymeric starting materials) encompass alternating, random, block, star block, segmented polymers, or combinations thereof (e.g., wherein certain portions of the molecule are alternating and certain portions are random). With respect to star block copolymers, it should  
30 be understood that the polymeric segments described herein could form at least a part of one or more atoms of the star, although the segment itself would not necessarily include the core branch point of the star.

Preferably, the polymers, and compounds used to make them, described herein have substantially no tertiary carbons in the main chain (i.e., backbone) of the molecules.

Methods of preparation of such polymers and compounds are 5 also provided.

As used herein, the terms "a," "an," "one or more," and "at least one" are used interchangeably.

As used herein, the term "aliphatic group" means a saturated or unsaturated linear (i.e., straight chain), cyclic, or branched organic 10 hydrocarbon. This term is used to encompass alkyl (e.g., -CH<sub>3</sub>, which is considered a "monovalent" group) (or alkylene if within a chain such as -CH<sub>2</sub>-, which is considered a "divalent" group), alkenyl (or alkenylene if within a chain), and alkynyl (or alkynylene if within a chain) groups, for example. The term "alkyl group" means a saturated linear or branched 15 hydrocarbon group including, for example, methyl, ethyl, isopropyl, t-butyl, heptyl, dodecyl, octadecyl, amyl, 2-ethylhexyl, and the like. The term "alkenyl group" means an unsaturated, linear or branched hydrocarbon group with one or more carbon-carbon double bonds, such as a vinyl group. The term "alkynyl group" means an unsaturated, linear 20 or branched hydrocarbon group with one or more carbon-carbon triple bonds. The term "aromatic group" or "aryl group" means a mono- or polynuclear aromatic organic hydrocarbon group. These hydrocarbon groups may be substituted with heteroatoms, which can be in the form of functional groups. The term "heteroatom" means an element other than 25 carbon (e.g., nitrogen, oxygen, sulfur, chlorine, etc.).

As used herein, a "biomaterial" may be defined as a material that is substantially insoluble in body fluids and tissues and that is designed and constructed to be placed in or onto the body or to contact fluid or tissue of the body. Ideally, a biomaterial will not induce undesirable 30 reactions in the body such as blood clotting, tissue death, tumor formation, allergic reaction, foreign body reaction (rejection) or inflammatory reaction; will have the physical properties such as strength, elasticity, permeability and flexibility required to function for the intended

purpose; can be purified, fabricated and sterilized easily; and will substantially maintain its physical properties and function during the time that it remains implanted in or in contact with the body. A "biostable" material is one that is not broken down by the body, whereas a

5 "biocompatible" material is one that is not rejected by the body.

- As used herein, a "medical device" may be defined as a device that has surfaces that contact blood or other bodily tissues in the course of their operation. This can include, for example, extracorporeal devices for use in surgery such as blood oxygenators, blood pumps, blood
- 10 sensors, tubing used to carry blood and the like which contact blood which is then returned to the patient. This can also include implantable devices such as vascular grafts, stents, electrical stimulation leads, heart valves, orthopedic devices, catheters, shunts, sensors, replacement devices for nucleus pulposus, cochlear or middle ear implants,
- 15 intraocular lenses, and the like.

#### Brief Description of the Drawing

Figure 1 lists examples of catalysts suitable for use in methods of the invention.

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#### Detailed Description of Illustrative Embodiments of the Invention

The present invention provides polymers (preferably, segmented polyurethanes), compounds used to prepare such polymers (preferably, the soft segments of segmented polymers), and medical devices that

25 include such polymers (preferably, biomaterials). Preferably, the polymers are generally resistant to oxidation and/or hydrolysis, particularly with respect to their backbones, as opposed to their side chains.

The polymers include one or more diorgano groups. These

30 diorgano (e.g., gem-dialkyl) groups are of the general formula  $-C(R^3)_2-$  wherein C is a quaternary carbon and each  $R^3$  is independently (i.e., may be the same or different) a saturated or unsaturated aliphatic group, an aromatic group, or combinations thereof, optionally including

heteroatoms (which may be in the chain of the organic group or pendant therefrom as in a functional group). Preferably, each R<sup>3</sup> is independently a straight chain alkyl group, optionally including heteroatoms. Most preferably, each R<sup>3</sup> is independently a straight chain alkyl group without heteroatoms.

- The polymers also include one or more silicon-containing groups. These silicon-containing groups are of the formula -Si(R)<sub>2</sub>-V<sub>r</sub>- wherein V is of the formula -O-Si(R)<sub>2</sub>- (thereby forming a siloxane group) or is R<sup>1</sup> (thereby forming a silane group). Each R is independently a saturated or unsaturated aliphatic group, an aromatic group, or combinations thereof, optionally including heteroatoms (which may be in the chain of the organic group or pendant therefrom as in a functional group). Each R<sup>1</sup> is independently a saturated or unsaturated aliphatic group, an aromatic group, or combinations thereof, optionally including heteroatoms (which may be in the chain of the organic group or pendant therefrom as in a functional group). Preferably, the aromatic groups of R<sup>1</sup> are within the backbone of the polymer chain.

Polymers of the present invention can be used in medical devices as well as nonmedical devices. Preferably, they are used in medical devices and are suitable as biomaterials. Examples of medical devices are listed above. Examples of nonmedical devices include foams, insulation, clothing, footwear, paints, coatings, adhesives, building construction materials, etc.

The polymers suitable for forming biomaterials for use in medical devices according to the present invention include quaternary carbons, silicon-containing groups, and are preferably polyurethanes, polyureas, or polyurethane-ureas. These polymers can vary from hard and rigid to soft and flexible. Preferably, the polymers are elastomers. An "elastomer" is a polymer that is capable of being stretched to approximately twice its original length and retracting to approximately its original length upon release.

Polymers of the present invention can be random, alternating, block, star block, segmented copolymers, or combinations thereof. Most

preferably, the polymers are segmented copolymers (i.e., containing both hard and soft domains or segments) and are comprised substantially of alternating relatively soft segments and relatively hard segments, although nonsegmented copolymers are also within the

5 scope of the present invention.

For segmented polymers, either the hard or the soft segments, or both, include a diorgano moiety and a silicon-containing moiety, thereby providing a polymer that has reduced susceptibility to oxidation and/or hydrolysis, at least with respect to the polymer backbone. As used

10 herein, a "hard" segment is one that is either crystalline at use temperature or amorphous with a glass transition temperature above use temperature (i.e., glassy), and a "soft" segment is one that is amorphous with a glass transition temperature below use temperature (i.e., rubbery). A crystalline or glassy moiety or hard segment is one that

15 adds considerable strength and higher modulus to the polymer. Similarly, a rubbery moiety or soft segment is one that adds flexibility and lower modulus, but may add strength particularly if it undergoes strain crystallization, for example. The random or alternating soft and hard segments are linked by urethane and/or urea groups and the

20 polymers may be terminated by hydroxyl, amine, and/or isocyanate groups.

As used herein, a "crystalline" material or segment is one that has ordered domains. A "noncrystalline" material or segment is one that is amorphous (a noncrystalline material may be glassy or rubbery). A

25 "strain crystallizing" material is one that forms ordered domains when a strain or mechanical force is applied.

An example of a medical device for which the polymers are particularly well suited is a medical electrical lead, such as a cardiac pacing lead, a neurostimulation lead, etc. Examples of such leads are

30 disclosed, for example, in U.S. Pat. Nos. 5,040,544 (Lessar et al.), 5,375,609 (Molacek et al.), 5,480,421 (Otten), and 5,238,006 (Markowitz).

## Polymers and Methods of Preparation

- A wide variety of polymers are provided by the present invention. They can be random, alternating, block, star block, segmented copolymers (or combinations thereof), preferably they are copolymers
- 5 (including terpolymers, tetrapolymers), that can include olefins, amides, esters, imides, epoxies, ureas, urethanes, carbonates, sulfones, ethers, acetals, phosphonates, and the like. These include moieties containing diorgano (preferably, gem-dialkyl) groups of the general formula -C(R<sup>3</sup>)<sub>2</sub>- wherein C is a quaternary carbon.
- 10 Such polymers can be prepared using a variety of techniques from polymerizable compounds (e.g., monomers, oligomers, or polymers) containing diorgano (preferably, gem-dialkyl) moieties of the general formula -C(R<sup>3</sup>)<sub>2</sub>- wherein C is a quaternary carbon, and/or silicon-containing moieties of the formula -Si(R)<sub>2</sub>-R<sup>1</sup>- (thereby forming a silane group) or -Si(R)<sub>2</sub>-(O-Si(R)<sub>2</sub>)- (thereby forming a siloxane group).
- 15 Such compounds include dienes, diols, diamines, or combinations thereof, for example.
- Although certain preferred polymers are described herein, the polymers used to form the preferred biomaterials in the medical devices
- 20 of the present invention can be a wide variety of polymers that include urethane groups, urea groups, or combinations thereof. Such polymers are prepared from isocyanate-containing compounds, such as polyisocyanates (preferably diisocyanates) and compounds having at least two functional groups reactive with the isocyanate groups, such as
- 25 polyols and/or polyamines (preferably diols and/or diamines). Any of these reactants can include a diorgano and/or silicon-containing moiety (preferably in the polymer backbone), although preferably a diorgano and/or silicon-containing moiety is provided by the polyols and/or polyamines, particularly diols and/or diamines (including the diols or
- 30 diamines of the dimer acid described below).

The presence of the diorgano moiety and silicon-containing moiety provides a polymer that is more resistant to oxidative and/or hydrolytic degradation but still has a relatively low glass transition

temperature (Tg). Furthermore, preferably, both the hard and soft segments are themselves substantially ether-free, ester-free, and carbonate-free polyurethanes, polyureas, or combinations thereof.

- Preferred polymers of the present invention include a group of the
- 5 formula  $-(R^1)_n-(-Z-(R^2)_m-)_p-$ , wherein -Z- is a diorgano moiety  $-C(R^3)_2-$ ,  
and a group of the formula  $-(-Si(R)_2-V_r-)_s-$  wherein V is of the formula  $-O-$   
 $Si(R)_2-$  (thereby forming a siloxane group) or is  $R^1$  (thereby forming a  
silane group). In one embodiment, particularly preferred polymers also  
include one or more urethane groups, urea groups, or combinations  
10 thereof (preferably, just urethane groups). In another embodiment,  
particularly preferred polymers are copolymers (i.e., prepared from two  
or more monomers, including terpolymers or tetrapolymers). Thus, the  
present invention provides polymers with these groups randomly  
distributed or ordered in blocks or segments.

- 15 Polymers of the present invention can be linear, branched, or  
crosslinked. This can be done using polyfunctional isocyanates or  
polyols (e.g., diols, triols, etc.) or using compounds having unsaturation  
or other functional groups (e.g., thiols) in one or more monomers with  
radiation crosslinking, for example. Such methods are well known to  
20 those of skill in the art.

Preferably, such polymers (and the compounds used to make  
them) have substantially no tertiary carbons in the main chain (i.e.,  
backbone).

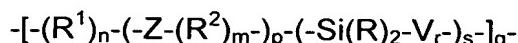
- In the quaternary-carbon group of the formula  $-(R^1)_n-(-Z-(R^2)_m-)_p-$ ,
- 25 n = 0 or 1; m = 0 or 1; p = 1-100,000; R<sup>1</sup> and R<sup>2</sup> are each independently  
a saturated or unsaturated aliphatic group, an aromatic group, or  
combinations thereof, optionally including heteroatoms (which may be in  
the chain of the organic group or pendant therefrom as in a functional  
group), preferably with the proviso that the aromatic groups are within  
30 the backbone; and Z is a diorgano moiety  $-C(R^3)_2-$  wherein each R<sup>3</sup> is  
independently a saturated or unsaturated aliphatic group, an aromatic  
group, or combinations thereof, optionally including heteroatoms (which  
may be in the chain of the organic group or pendant therefrom as in a

functional group), wherein the two R<sup>3</sup> groups within a -C(R<sup>3</sup>)<sub>2</sub>- moiety can be optionally joined to form a ring. It should be understood that the repeat units -Z-(R<sup>2</sup>)<sub>m</sub>- can vary within any one molecule.

In the silicon-containing group of the formula -Si(R)<sub>2</sub>-V<sub>r</sub>-, r = 0-

- 5 100,000; s = 1-100,000, V is of the formula -O-Si(R)<sub>2</sub>- (thereby forming a siloxane group) or is R<sup>1</sup> (thereby forming a silane group). Each R is independently a saturated or unsaturated aliphatic group, an aromatic group, or combinations thereof, optionally including heteroatoms (which may be in the chain of the organic group or pendant therefrom as in a functional group). Each R<sup>1</sup> group is as defined above.
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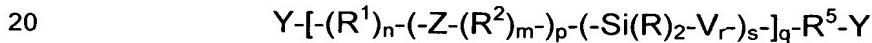
Preferred polymers include a group of the formula



- wherein each of the numerical variables (n, m, p, r, and s) and the organic groups (R, R<sup>1</sup>, and R<sup>2</sup>) and the V group are as defined above. In
- 15 this formula q = 1-100,000.

A preferred source of the group of the formula

-[(R<sup>1</sup>)<sub>n</sub>-(-Z-(R<sup>2</sup>)<sub>m</sub>)<sub>p</sub>-(-Si(R)<sub>2</sub>-V<sub>r</sub>)<sub>s</sub>-]<sub>q</sub>- is a compound (typically a polymeric starting compound) of the formula (Formula I):



- wherein: each Y is independently OH or NR<sup>4</sup>H; n = 0 or 1; m = 0 or 1; p = 1-100,000; r = 0-100,000; s = 1-100,000; q = 1-100,000 (preferably q = 1); R<sup>1</sup>, R<sup>2</sup>, and R<sup>5</sup> are each independently a saturated or unsaturated aliphatic group, an aromatic group, or combinations thereof, optionally including heteroatoms, preferably with the proviso that the aromatic groups are within the backbone; Z is a diorgano moiety -C(R<sup>3</sup>)<sub>2</sub>- wherein each R<sup>3</sup> is independently a saturated or unsaturated aliphatic group, an aromatic group, or combinations thereof, optionally including heteroatoms, wherein the two R<sup>3</sup> groups within a -C(R<sup>3</sup>)<sub>2</sub>- moiety can be optionally joined to form a ring; each R is independently a saturated or unsaturated aliphatic group, an aromatic group, or combinations thereof, optionally including heteroatoms; each R<sup>4</sup> is independently H or a
- 25
  - 30

saturated or unsaturated aliphatic group, an aromatic group, or combinations thereof; and V is -O-Si(R)<sub>2</sub>- or R<sup>1</sup>.

- It should be understood that any repeat unit can vary within any one molecule. For example, in addition to each R being the same or
- 5 different within each Si(R)<sub>2</sub> group, the Si(R)<sub>2</sub> groups (if repeated) can be the same or different in any one molecule. Also, in addition to each R<sup>2</sup> being the same or different within each Z(R<sup>2</sup>)<sub>m</sub> group, the Z(R<sup>2</sup>)<sub>m</sub> groups (if repeated) can be the same or different in any one molecule.
- Furthermore, each R<sup>1</sup> (if repeated) can be the same or different in any
- 10 one molecule.

The R<sup>3</sup> groups on the quaternary carbon (in the Z groups) are preferably selected such that the ultimate product (e.g., a segmented polyurethane polymer) has one or more of the following properties (preferably, all of the following properties) relative to a polymer without

15 the diorgano (Z) moieties: reduced glass transition temperature (Tg) of the polymer; enhanced strength as a result of hydrogen bonding between the polymer chains; suppressed crystallization of soft segments at room temperature under zero strain; increased strain crystallization; greater ability to control phase separation for balancing elastomeric

20 properties versus strength; greater ability to control melt rheology; and greater ability to modify the polymers using functional groups within the R<sup>3</sup> groups.

Although the diorgano moieties reduce the susceptibility of the compound of Formula I and the ultimate polymer to oxidation or

25 hydrolysis, the R<sup>3</sup> groups could themselves be susceptible to oxidation or hydrolysis as long as the main chain (i.e., the backbone) is not generally susceptible to such reactions. Preferably, the R<sup>3</sup> groups are each independently a straight chain alkyl group, an aryl group, or combinations thereof. More preferably, the R<sup>3</sup> groups are each

30 independently a straight chain alkyl group.

Optionally, the R<sup>3</sup> groups can include heteroatoms, such as nitrogen, oxygen, phosphorus, sulfur, and halogen. These could be in the chain of the organic group or pendant therefrom in the form of

- functional groups, as long as the polymer is generally resistant to oxidation and/or hydrolysis, particularly with respect to its backbone, as opposed to its side chains. Such functional groups include, for example, an alcohol, ether, acetoxy, ester, aldehyde, acrylate, amine, amide,
- 5 imine, imide, and nitrile, whether they be protected or unprotected. Most preferably, each R<sup>3</sup> is independently a straight chain alkyl group without heteroatoms.

The R groups on the silicon atoms are preferably selected such that the ultimate product (e.g., a segmented polyurethane polymer) has

10 one or more of the following properties (preferably, all of the following properties) relative to a polymer without the silicon-containing moieties: greater chain flexibility; less susceptibility to oxidation and hydrolysis; and greater ability to modify the polymers using functional groups within the R groups.

15 Although the silicon-containing moieties reduce the susceptibility of the compound of Formula I and the ultimate polymer to oxidation or hydrolysis, the R groups could themselves be susceptible to oxidation or hydrolysis as long as the main chain (i.e., backbone) is not generally susceptible to such reactions. Preferably, the R groups are each

20 independently a straight, branched, or cyclic alkyl or alkenyl group, a phenyl group, or a straight chain or branched alkyl substituted phenyl group. More preferably, each R group is a straight chain alkyl group.

Optionally, the R groups can include heteroatoms, such as nitrogen, oxygen, phosphorus, sulfur, and halogen. These could be in

25 the chain of the organic group or pendant therefrom in the form of functional groups, as long as the polymer is generally resistant to oxidation and/or hydrolysis, particularly with respect to its backbone, as opposed to its side chains. Such functional groups include, for example, an alcohol, ether, acetoxy, ester, aldehyde, acrylate, amine, amide,

30 imine, imide, and nitrile, whether they be protected or unprotected. Most preferably, each R is independently a straight chain alkyl group without heteroatoms.

- Preferably, R<sup>1</sup> and R<sup>2</sup> are each independently a straight chain alkylene group (e.g., a divalent aliphatic group such as –CH<sub>2</sub>-CH<sub>2</sub>- and the like), an arylene group, or combinations thereof, preferably with the proviso that the aromatic groups are within the backbone. More
- 5 preferably, R<sup>1</sup> and R<sup>2</sup> do not include tertiary carbon atoms in the main chain (i.e., backbone) of the molecule. Most preferably, R<sup>1</sup> and R<sup>2</sup> are each independently a straight chain alkylene group.
- Preferably, each R<sup>4</sup> group is independently hydrogen, a straight chain alkyl group, an aryl group, or combinations thereof. More
- 10 preferably, each R<sup>4</sup> group is independently hydrogen or a straight chain alkyl group.
- The R, R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, and R<sup>4</sup> groups are selected such that the number average molecular weight of a compound of Formula I is no greater than about 100,000 grams per mole (g/mol or Daltons).
- 15 Preferably, the molecular weight is about 1000 g/mol to about 1500 g/mol.
- Preferably, R, R<sup>1</sup>, and R<sup>2</sup> are each independently an organic group that includes at least one carbon atom, and more preferably at least two carbon atoms. Preferably, R, R<sup>1</sup>, and R<sup>2</sup> are each
- 20 independently an organic group that includes no more than (i.e., up to) 100 carbon atoms, more preferably no more than 50 carbon atoms, and most preferably no more than 20 carbon atoms.
- Preferably, R<sup>3</sup> is an organic group that includes at least one carbon atom. Preferably, R<sup>3</sup> is an organic group that includes no more
- 25 than 100 carbon atoms, more preferably no more than 50 carbon atoms, and most preferably no more than 20 carbon atoms.
- Preferably, R<sup>4</sup> is hydrogen or an organic group that includes at least one carbon atom. Preferably, if R<sup>4</sup> is an organic group, it includes no more than 100 carbon atoms, more preferably no more than 50
- 30 carbon atoms, even more preferably no more than 20 carbon atoms, and most preferably no more than 4 carbon atoms. Most preferably, R<sup>4</sup> is hydrogen.

The values for n, m, p, r, s, and q are average values. Preferably, at least one n or m is one. More preferably, both n and m are one. In increasing order of preference, p, s, and q are each independently 1-100,000, 1-50,000, 1-10,000, 1-5000, 1-2000, 1-1000, 1-500, 1-200,

- 5 1-100, 1-50, 1-20, 2-20, and 2-12. Preferably, q = 1 for the starting compound of Formula I. In increasing order of preference, r is 0-100,000, 0-200, and 0-20.

Preferably, the Y groups are OH or NH<sub>2</sub>. More preferably, the Y groups are both OH.

- 10 The polymers of the present invention can be prepared using standard techniques. Certain polymers can be made using one or more of the compounds of Formula I. Typically, a compound of Formula I is combined with an organic compound containing two or more groups capable of reacting with hydroxyl or amine groups.

- 15 For example, if Y in Formula I is an amine (NR<sup>4</sup>H), one could react those amines with di-, tri- or poly(acids), di-, tri, or poly(acyl chlorides), or with cyclic amides (lactams) to form poly(amides). Alternatively, one could react those amines with di-, tri- or poly(anhydrides) to make poly(imides). Alternatively, one could react
- 20 those amines with glycidyl-containing compounds to form epoxies.

- If Y in Formula I is hydroxyl (OH), one could react those hydroxyl groups with di-, tri-, or poly(acids), di-, tri-, or poly(acyl chlorides), or with cyclic esters (lactones) to form poly(esters). Alternatively, one could react those hydroxyl groups with vinyl ether-containing compounds to
- 25 make poly(acetals). Alternatively, one could react those hydroxyls with sodium hydroxide to form sodium salts, and further react those salts with phosgene to form poly(carbonates). Reacting those sodium salts with other alkyl halide containing moieties can lead to poly(sulfones) and poly(phosphates) and poly(phosphonates).

- 30 Typically, the preferred urethane- and/or urea-containing polymers are made using polyisocyanates and one or more compounds of Formula I. It should be understood, however, that diols or diamines that do not contain such diorgano or silicon-containing moieties can also

be used to prepare the urethane- and/or urea-containing polymers of the present invention, as long as the resultant polymer includes at least some diorgano and silicon-containing moieties either from diols or diamines or other reactants. Also, other polyols and/or polyamines can

- 5 be used, including polyester, polyether, and polycarbonate polyols, for example, although such polyols are less preferred because they produce less biostable materials. Furthermore, the polyols and polyamines can be aliphatic, cycloaliphatic, aromatic, heterocyclic, or combinations thereof.

10 Examples of suitable polyols (typically diols) include those commercially available under the trade designation POLYMEG and other polyethers such as polyethylene glycol and polypropylene oxide, polybutadiene diol, dimer diol (e.g., that commercially available under the trade designation DIMEROL (Unichema North America of Chicago,

- 15 IL), polyester-based diols such as those commercially available from STEPANPOL (from Stepan Corp., Northfield, IL), CAPA (a polycaprolactone diol from Solvay, Warrington, Cheshire, United Kingdom), TERATE (from Kosa, Houston, TX), poly(ethylene adipate) diol, poly(ethylene succinate) diol, poly(1,4-butanediol adipate) diol,
- 20 poly(caprolactone) diol, poly(hexamethylene phthalate) diol, and poly(1,6-hexamethylene adipate) diol, as well as polycarbonate-based diols such as poly(hexamethylene carbonate) diol.

Other polyols can be used as chain extenders in the preparation of polymers, as is conventionally done in the preparation of

- 25 polyurethanes, for example. Examples of suitable chain extenders include 1,10-decanediol, 1,12-dodecanediol, 9-hydroxymethyl octadecanol, cyclohexane-1,4-diol, cyclohexane-1,4-bis(methanol), cyclohexane-1,2-bis(methanol), ethylene glycol, diethylene glycol, 1,3-propylene glycol, dipropylene glycol, 1,2-propylene glycol, trimethylene
- 30 glycol, 1,2-butylene glycol, 1,3-butanediol, 2,3-butanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,2-hexylene glycol, 1,2-cyclohexanediol, 2-butene-1,4-diol, 1,4-cyclohexanedimethanol, 2,4-dimethyl-2,4-pentanediol, 2-methyl-2,4-pentanediol, 1,2,4-butanetriol,

2-ethyl-2-(hydroxymethyl)-1,3-propanediol, glycerol, 2-(hydroxymethyl)-1,3-propanediol, neopentyl glycol, pentaerythritol, and the like.

Examples of suitable polyamines (typically diamines) include ethylenediamine, 1,4-diaminobutane, 1,10-diaminodecane,

- 5 1,12-diaminododecane, 1,8-diaminoctane, 1,2-diaminopropane, 1,3-diaminopropane, tris(2-aminoethyl)amine, lysine ethyl ester, and the like.

Examples of suitable mixed alcohols/amines include 5-amino-1-pentanol, 6-amino-1-hexanol, 4-amino-1-butanol, 4-aminophenethyl

- 10 alcohol, ethanolamine, and the like.

Suitable isocyanate-containing compounds for preparation of polyurethanes, polyureas, or polyurethanes-ureas, are typically aliphatic, cycloaliphatic, aromatic, and heterocyclic (or combinations thereof) polyisocyanates. In addition to the isocyanate groups they can include

- 15 other functional groups such as biuret, urea, allophanate, uretidine dione (i.e., isocyanate dimer), and isocyanurate, etc., that are typically used in biomaterials. Suitable examples of polyisocyanates include 4,4'-diisocyanatodiphenyl methane (MDI), 4,4'-diisocyanatodicyclohexyl methane (HMDI), cyclohexane-1,4-diisocyanate, cyclohexane-1,2-diisocyanate, isophorone diisocyanate, tolylene diisocyanates, naphthylene diisocyanates, benzene-1,4-diisocyanate, xylene diisocyanates, trans-1,4-cyclohexylene diisocyanate, 1,4-diisocyanatobutane, 1,12-diisocyanatododecane, 1,6-diisocyanatohexane, 1,5-diisocyanato-2-methylpentane, 4,4'-methylenebis(cyclohexyl isocyanate), 4,4'-methylenebis(2,6-diethylphenyl isocyanate), 4,4'-methylenebis(phenyl isocyanate), 1,3-phenylene diisocyanate, poly((phenyl isocyanate)-co-formaldehyde), tolylene-2,4-diisocyanate, tolylene-2,6-diisocyanate, dimer diisocyanate, as well as polyisocyanates available under the trade designations
- 20
- 25
- 30 DESMODUR RC, DESMODUR RE, DESMODUR RFE, and DESMODUR RN from Bayer, and the like.

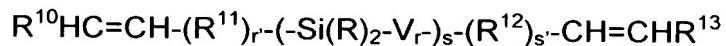
The relatively hard segments of the polymers of the present invention are preferably fabricated from short to medium chain

diisocyanates and short to medium chain diols or diamines, all of which preferably have molecular weights of less than about 1000 g/mol. Appropriate short to medium chain diols, diamines, and diisocyanates include straight chain, branched, and cyclic aliphatics, although 5 aromatics can also be used. Examples of diols and diamines useful in these more rigid segments include both the short and medium chain diols or diamines discussed above.

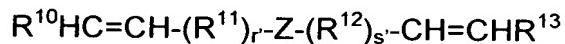
In addition to the polymers described herein, biomaterials of the invention can also include a variety of additives. These include, 10 antioxidants, colorants, processing lubricants, stabilizers, imaging enhancers, fillers, and the like.

#### Starting Materials and Methods of Preparation

The novel compounds of Formula I above can be made by the 15 synthetic route described in the Examples Section. The method typically includes combining monomers of Formula II

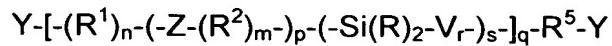


20 or Formula III



(which are described in greater detail below) with an alkene metathesis 25 catalyst and optionally applying a vacuum. This typically involves a novel intermediate in which Y is a protected group such as an acetoxy (-OC(O)CH<sub>3</sub>), a benzyl ether (-OCH<sub>2</sub>phenyl), a tertiary butyl carbamate (-NR<sup>4</sup>-C(O)-t-butyl), or a benzyl carbamate (-NR<sup>4</sup>-C(O)OCH<sub>2</sub>phenyl).

Thus, the present invention provides a polymeric starting compound of the formula (Formula I):



5

as described above.

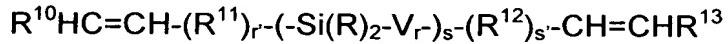
Preferably, the present invention provides a compound of the Formula I wherein: each Y is independently OH; each of the R groups are straight chain saturated alkyls or alkynes having 1-20 carbon  
10 atoms; and each of p, s, and q are 1-50.

Such compounds can be made starting with a diene compound having a quaternary carbon (i.e., a diorgano group referred to herein as Z or a -C(R<sup>3</sup>)<sub>2</sub>- group), a diene with a silicon-containing compound, a chain transfer agent, and optionally a chain extender. The dienes could  
15 be the same compounds, such that one diene includes both quaternary carbon and silicon. The diene compounds are polymerized, optionally with a chain extender, in the presence of an ADMET (Acyclic Diene Metathesis) catalyst followed by incorporation of a chain transfer agent yielding an unsaturated telechelic polymer.

20 The two carbon-carbon double bonds of the diene compound can be either internal or terminal as long as they are separated by the Z group.

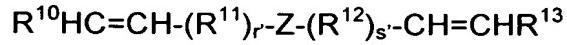
Preferably, the diene with the silicon is a compound of the formula (Formula II):

25



and the diene with the quaternary carbon is a compound of the formula (Formula III):

30



wherein: r, s, V, and R are as defined above; r' = 0 or 1; s' = 0 or 1; Z is a  $-C(R^3)_2-$  group as defined above;  $R^{10}$  and  $R^{13}$  are each independently hydrogen or straight chain, branched, or cyclic alkyl groups containing up to 6 carbon atoms; and  $R^{11}$  and  $R^{12}$  are each independently a

- 5 saturated aliphatic group, an aromatic group, or combinations thereof,  
preferably with the proviso that the aromatic groups are within the chain.  
Preferably, using this synthetic procedure R<sup>3</sup> does not include  
unsaturated aliphatic groups, although it can include aromatic groups.  
The resultant polymers, however, could be subsequently modified to  
10 include aliphatic unsaturation.

Preferably, R<sup>11</sup> and R<sup>12</sup> are each independently a straight chain alkylene group, an arylene group, or combinations thereof, preferably with the proviso that the aromatic groups are within the chain. More

- 15 group. Preferably, R<sup>11</sup> and R<sup>12</sup> are each independently an organic group that includes at least one carbon atom, and more preferably at least two carbon atoms. Preferably, R<sup>11</sup> and R<sup>12</sup> are each independently an organic group that includes no more than 100 carbon atoms, more preferably no more than 50 carbon atoms, and most preferably no more than 20 carbon atoms. Preferably, at least one of r' or s' is one. More preferably, both r' and s' are one.

A chain extender can be optionally used to alter the spacing between the Z groups in the resultant polymer. This also has the added advantage of allowing for a broader range of glass transition

- 25 temperatures ( $T_g$ 's) than can normally be realized upon polymerizing one monomer. The chain extender is a diene wherein the two carbon-carbon double bonds are either internal or terminal. Preferably, it is a compound of the formula (Formula IV):

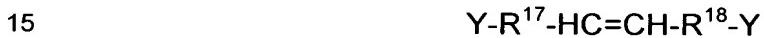
30  $R^{14}HC=CH-R^{15}-CH=CHR^{16}$

wherein: R<sup>14</sup> and R<sup>16</sup> are each independently hydrogen or straight chain, branched, or cyclic alkyl groups containing up to 6 carbon atoms; and

$R^{15}$  is a saturated aliphatic group, an aromatic group, or combinations thereof, preferably with the proviso that the aromatic groups are within the chain.

- Preferably,  $R^{15}$  is a straight chain alkylene group, an arylene group, or combinations thereof, preferably with the proviso that the aromatic groups are within the chain. More preferably,  $R^{15}$  is a straight chain alkylene group. Preferably,  $R^{15}$  is an organic group that includes at least one carbon atom, and more preferably at least two carbon atoms. Preferably,  $R^{15}$  is an organic group that includes no more than 100 carbon atoms, more preferably no more than 50 carbon atoms, and most preferably no more than 20 carbon atoms.

The chain transfer agent includes protecting groups and is preferably a compound of the formula (Formula V):



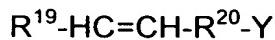
wherein: each Y is independently a protected form of an OH or an  $NR^4H$  group (e.g., wherein Y is an acetoxy, a benzyl ether, a tertiary butyl carbamate, or a benzyl carbamate);  $R^{17}$  and  $R^{18}$  are each independently a saturated aliphatic group, an aromatic group, or combinations thereof, preferably with the proviso that the aromatic groups are within the chain.

- Preferably,  $R^{17}$  and  $R^{18}$  are each independently a straight chain alkylene group, an arylene group, or combinations thereof, preferably with the proviso that the aromatic groups are within the chain. More preferably,  $R^{17}$  and  $R^{18}$  are each independently a straight chain alkylene group. Preferably,  $R^{17}$  and  $R^{18}$  are each independently an organic group that includes at least one carbon atom, and more preferably at least two carbon atoms. Preferably,  $R^{17}$  and  $R^{18}$  are each independently an organic group that includes no more than 100 carbon atoms, more preferably no more than 50 carbon atoms, and most preferably no more than 20 carbon atoms.

Alternatively, the chain transfer agent can include one alkene group and only one protected alcohol or amine. The alkene can be

terminal or, if not terminal, it can include a relatively small alkyl substituent that forms a volatile compound under the metathesis conditions. An example of this type of chain transfer agent is 10-undecene-1-yl-acetate. Such a compound is generally of the formula

5 (Formula VI):



wherein: Y is a protected form of an OH or an NR<sup>4</sup>H group (e.g.,

10 wherein Y is an acetoxy, a benzyl ether, a tertiary butyl carbamate, or a benzyl carbamate); R<sup>19</sup> and R<sup>20</sup> are each independently a saturated aliphatic group, an aromatic group, or combinations thereof, preferably with the proviso that the aromatic groups are within the chain; R<sup>19</sup> can also be hydrogen. Preferably, R<sup>19</sup> is a (C1-C6)alkyl group, and more  
15 preferably R<sup>19</sup> is H. If a compound of Formula VI is reacted with a compound of Formula III, the metathetic by-product would be of the formula R<sup>10</sup>HC=CHR<sup>19</sup>, which should have sufficiently small R<sup>10</sup> and R<sup>19</sup> groups to be volatile under the conditions of the polymerization reaction.

The ADMET catalyst can be any of a variety of catalysts capable  
20 of effecting metathesis polymerization. Examples include Schrock's molybdenum alkylidene catalyst, Grubbs' ruthenium benzylidene catalyst, and Grubbs' imidazolium catalyst, as shown in Figure 1, which are well known to those of skill in the art.

Preferably, the quaternary carbon-containing and silicon-  
25 containing diene compound(s) are combined with an ADMET catalyst under conditions effective to cause polymerization to a high molecular weight intermediate (e.g., a number average molecular weight of about 10,000 g/mol to about 1 x 10<sup>6</sup> g/mol). Optionally, a chain extender can be added before the catalyst is added. Typically, conditions of this  
30 polymerization include reduced pressure (e.g., less than about 10 milliTorr (1.33 pascals)) at a temperature of about 0°C to about 100°C (preferably, about 25°C to about 60°C) and a time of about 1 hour to about 10 days (preferably, about 48 hours to about 120 hours). The

reduced pressure is desired to remove metathetic by-products and reduce the number of terminal olefins. This high molecular weight intermediate can be stored for later reaction if desired.

- This high molecular weight intermediate is then combined with a
- 5 chain transfer agent in the presence of the same or a different ADMET catalyst under conditions effective to depolymerize the high molecular weight intermediate and form an unsaturated telechelic polymer. Typically, such conditions include an inert atmosphere (e.g., argon) or under reduced pressure (e.g., less than about 10 milliTorr ( $1.32 \times 10^{-5}$  atmospheres or 1.33 pascals (Pa)) and a temperature of about 0°C to about 100°C (preferably, about 50°C to 60°C) and a time of about 1 hour to about 10 days (preferably, about 24 hours to about 96 hours). The amount of chain transfer agent controls the molecular weight of the unsaturated telechelic polymer. Optionally, this depolymerization
- 10 reaction is carried out in an organic solvent (e.g., toluene) to reduce the viscosity.
- 15

- Optionally, the unsaturated telechelic polymer could be formed in a one-step reaction in which the quaternary carbon-containing and silicon-containing diene compound(s), optional chain extender, and a
- 20 chain transfer agent are combined prior to the addition of the ADMET catalyst to the mixture. This may or may not be carried out in an organic solvent.

- The unsaturated telechelic polymer is then subjected to a hydrogenation reaction. This is preferably carried out in the presence of
- 25 a hydrogenation catalyst under conditions effective to form a fully saturated telechelic polymer. The hydrogenation catalyst is preferably palladium on activated carbon, but could be others well known in the art. Typically, such conditions include the use of a hydrogen pressure of about 1 psig (0.068 atmospheres, 6.89 Pa) to about 1000 psig (68
- 30 atmospheres, 6.89 MPa) (preferably, about 300 psig (20 atmospheres, 2.03 MPa) to about 500 psig (34 atmospheres, 3.45 MPa)) and a temperature of about 0°C to about 200°C (preferably, about 60°C to

about 100°C) and a time of about 1 hour to about 10 days (preferably, about 3 days to about 5 days).

- Alternatively, the hydrogenation reaction can be carried out using para-toluenesulfonhydrazide in the presence of a base (typically, 5 tributylamine) in a refluxing organic solvent such as xylene.

The saturated telechelic polymer is then deprotected using a reaction scheme specific to the protecting group used. For example, if the protecting group is an acetate, the polymer is hydrolyzed under conditions effective to convert the acetate end groups to hydroxyl 10 groups. Typically, such conditions include the use of sodium methoxide in an organic solvent (e.g., methanol) at a temperature of about 0°C to about 100°C (preferably, about 0°C to about 25°C) and a time of about 1 minute to about 1 day (preferably, about 4 hours to about 1 day).

Alternatively, the unsaturated telechelic polymer could be 15 deprotected prior to being hydrogenated to the saturated telechelic polymer.

The invention has been described with reference to various specific and preferred embodiments and will be further described by 20 reference to the following detailed examples. It is understood, however, that there are many extensions, variations, and modification on the basic theme of the present invention beyond that shown in the examples and detailed description, which are within the spirit and scope of the present invention.

25

### Examples

All glassware was dried prior to use. All reactions were performed in a nitrogen or argon atmosphere unless otherwise noted. 30 Hexanes, chloroform, sodium hydroxide, AMBERLITE IRC-718 ion exchange resin, ALIQUOT 336, anhydrous magnesium sulfate, silica gel, activated neutral alumina, toluene, dibutyltin dilaurate, tetrahydrofuran (THF), dioxane, and 10% palladium on activated carbon

are all available from Sigma-Aldrich, Milwaukee, WI. Prior to use, the AMBERLITE IRC-718 ion exchange resin beads were dried using a rotary evaporator. Tricyclohexylphosphine[1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene][benzylidene]ruthenium(IV) dichloride (Grubbs' imidazolium metathesis catalyst) was purchased from Strem Chemicals Inc., Newburyport, MA, and stored at -30°C in an argon atmosphere glovebox until used. The source of 10-undecen-1-yl acetate was Bedoukian Research, Incorporated, Danbury, CT. The source of 1,4-butanediol (BDO) was Mitsubishi Chemical, America, Inc., White Plains, NY. The source of solid, flaked 4,4'-methylenebis(phenylisocyanate) (MDI) was Bayer Corporation, Pittsburgh, PA, and sold as fused MONDUR M. The temperatures reported for metathesis reactions were measured using a thermocouple placed between the flask and the heating mantle.

6,6-Dimethyl-1,10-undecadiene was synthesized as described in Example 1 of U.S. Application Publication No. 2003-0125499, published on July 3, 2003.

Synthesis of 7,7-Diethyl-7-silyl-1,12-tridecadiene: One hundred grams of 1,5-hexadiene (Aldrich) was placed in a 500-milliliter round-bottomed three-neck flask. The flask was outfitted with a magnetic stirbar, heating mantle, water-cooled condenser, thermocouple, and addition funnel. The flask was heated with stirring. Meanwhile, the addition funnel was charged with 25 milliliters diethylsilane (Aldrich) and 200 grams 1,5-hexadiene. Two milliliters of a platinum-divinyltetramethyldisiloxane complex in xylene (2-3% Pt) (United Chemical Technologies, Bristol, PA) was added to the flask. The mixture in the addition funnel was added dropwise when the contents of the flask reached 40°C. A small exotherm was observed. After the 25 addition was complete, the mixture was stirred overnight at 40°C. The reaction mixture was then transferred to a one-liter single-neck round-bottomed flask and the excess 1,5-hexadiene was removed using a rotary evaporator. The contents of the flask were then diluted with five

volumes of hexanes and dried AMBERLITE IRC-718 ion exchange resin beads were added to sequester the platinum. The reaction mixture was then further purified by passage through a 1.5-cm diameter chromatography column to which had been added about 15 cm of silica gel, followed by 15 centimeters (cm) of activated neutral alumina.

5 Additional hexane was used to elute the product until a sample of eluent evaporated on a watchglass left no residue.

Example 1: Synthesis of an unsaturated copolymer containing *gem*-dimethyl and diethylsilane moieties

10 Into a 250 milliliter (mL) round-bottomed flask, 16.9 grams (g) 6,6-dimethyl-1,10-undecadiene and 94.72 g 7,7-diethyl-7-silyl-1,12-tridecadiene were added. The solution was sparged with nitrogen for 30 minutes. The flask was transferred to a nitrogen-atmosphere glovebox

15 and 0.21 g of tricyclohexylphosphine[1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene][benzylidene]ruthenium(IV) dichloride (Grubbs' imidazolium catalyst) was added. The light red solution was magnetically stirred and vacuum was applied. The solution began bubbling as ethylene was released. The pressure within the flask

20 stabilized at 65 Pascals (Pa), and the temperature of the reaction was 33°C. After 88 hours, the solution was brown in color, no bubbles were observed, and the pressure within the flask was 7 Pa. The temperature was raised to 60°C and upon heating, the pressure rose to 22 Pa. The pressure dropped to 6 Pa after 137 hours of reaction time. The reaction

25 flask was removed from the glovebox and 150 mL hexanes and 17 g dried AMBERLITE IRC-718 ion exchange resin was added. The mixture was magnetically stirred slowly until the dark brown solution became lighter in color. An additional 12 g of the dried AMBERLITE ion exchange resin was added. The solution became pale orange in color.

30 The ion exchange resin was removed by filtration using a Buechner funnel with Whatman Number 2 filter paper. Addition hexanes were used to transfer the product from the Erlenmeyer flask to a one-liter round-bottomed flask. Most of the hexanes were removed by rotary

evaporation. The product was passed through a fritted glass column in which had been placed sequentially sand (0.5 cm), silica (4 cm), activated neutral alumina (4 cm), and an additional layer of sand (0.5 cm). The pale orange product became clear and colorless upon elution

5 through the column.

To build a higher molecular weight polymer, the product was treated a second time with catalyst. Inside the nitrogen-atmosphere glovebox, 0.27 g Grubbs' imidazolium catalyst was added to the flask. Bubbling was observed and the pressure was 933 Pa. The reaction

10 temperature was 33°C for 16 hours and then was increased to 60°C.

The brown solution had become more viscous and large bubbles were forming. After 96 hours of reacting at 60°C, bubbles were still observed and the pressure was 2.5 Pa. After an additional 24 hours, no more bubbles were observed and the flask was removed from the glovebox.

15 Hexanes (200 mL) and 26 g dried AMBERLITE IRC-718 ion exchange resin were added to the brown polymer. The mixture was stirred for three hours and the color changed from dark to light brown. An additional 13 g of the dried ion exchange resin was added and the solution was stirred until it became lighter in color. The Amberlite was

20 filtered using a Buechner funnel with Whatman Number 40 filter paper.

The solution was further purified by passage through a column as described in the previous step. The hexanes were removed by rotary evaporation. The final yield was 77.82 g. The NMR data indicated that there were 18.3 repeat groups on average, and the molecular weight

25 was calculated to be 4355 g/mol.

The signals observed by proton NMR were: δ 5.8, 5.5-5.3, 5.0, 2.0, 1.65, 1.4-1.2, 0.9, 0.8, 0.6-0.4 ppm. The signals observed by <sup>13</sup>C NMR were: δ 130, 36.9, 34.1, 33.9, 32.3, 24.2, 23.6, 23.4, 11.7, 7.5, and 3.8 ppm.

30 The absorbances observed by FTIR were: 2951, 2874, 2852, 1640, 1457, 1414, 1377, 1340, 1304, 1235, 1168, 1013, 965, 909, 850, 753, and 720 cm<sup>-1</sup>.

**Example 2: Hydrogenation of the copolymer of Example 1**

The copolymer of Example 1 (23.75 g) was hydrogenated using a Parr pressure reactor. The hydrogenation was performed at 4.14 MPa and 60°C using 10% Pd/C as catalyst to obtain the fully hydrogenated 5 copolymer. Toluene was used as solvent. The reaction was continued until there was no further uptake of hydrogen. The signals observed by proton NMR were: δ 1.4-1.2, 0.9 (t), 0.8 (s), 0.6-0.4 ppm.

**Example 3: Synthesis of an acetoxytelechelic copolymer containing**

10 **gem-dimethyl and diethylsilane moieties**

A portion of the unsaturated copolymer (54.07 g) of Example 1 was transferred to a 500 mL single-neck, round-bottomed flask. To this flask, 25.5 g 1,20-diacetoxyeicosa-10-ene were added. In a nitrogen-atmosphere glovebox, the mixture was heated to 60°C and stirred until a 15 homogenous solution formed. The solution became clear and colorless, at which time 0.13 g Grubbs' imidazolium catalyst was added. The solution was magnetically stirred and vacuum was applied. The pressure within the flask decreased to 104 Pa and vigorous bubbling was observed. After 18.5 hours, the pressure was 2 Pa and bubbles 20 were no longer observed. The flask was removed from the glovebox and 120 mL hexanes and 26 g dried AMBERLITE IRC-718 were added. The solution was stirred until it became lighter in color. The AMBERLITE was filtered using a Buechner funnel with Whatman Number 40 filter paper. The solution was sent through a column set up 25 as described in Example 1. After elution through the column, the hexanes were removed from the polymer solution by rotary-evaporation. This provided 73.54 g of acetoxytelechelic copolymer, a yellow, slightly viscous liquid.

The signals observed by proton NMR were: δ 5.5-5.3, 4.05 (t), 30 2.05 (s), 2.1-1.9, 1.65, 1.4-1.2, 0.9, 0.8, 0.6-0.4 ppm. The signals observed by <sup>13</sup>C NMR were: δ 171.3, 130, 64.7, 33.9, 32.7, 32.3, 29.6, 29.4, 28.7, 26.0, 23.4, 11.7, 7.5, and 3.8 ppm.

The absorbances observed by FTIR were: 2951, 2874, 2852, 1744, 1458, 1415, 1386, 1364, 1237, 1169, 1036, 1014, 966, 851, 753, 721, and 605 cm<sup>-1</sup>.

5 Example 4: Synthesis of an unsaturated hydroxytelechelic copolymer containing *gem*-dimethyl and diethylsilane moieties

To a one-liter round-bottomed flask containing 73.54 g of the acetoxy-functional copolymer of Example 3, 160 mL hexanes, 83 g of 50% NaOH solution and 4.43 g ALIQUOT 336 were added. The solution 10 was magnetically stirred and brought to reflux. After 2.5 hours, the deprotection was complete, as observed by FTIR. The solution was transferred to a one liter separatory funnel. The organic layer was rinsed with water until the pH was neutral. A total of 3 Liters of wash water was used before a neutral pH was obtained. Approximately 100 15 mL chloroform was added to the separatory funnel to help dissipate the emulsion that had formed. The organic layer was transferred to a one liter Erlenmeyer flask and magnesium sulfate was added to the flask to dry the solution. The anhydrous magnesium sulfate was filtered using a Buechner funnel and Whatman Number 2 filter paper. The solution was 20 then transferred to a one liter round-bottomed flask and the hexanes were removed by rotary-evaporation. The product was transferred to a 500 mL round-bottomed flask, using a small amount of hexanes to ensure complete transfer, which were again removed by rotary- 25 evaporation. The result was 65.71 g hazy brown unsaturated hydroxytelechelic copolymer containing *gem*-dimethyl and diethylsilane moieties. The molecular weight of the diol was calculated by NMR to be 1322 g/mol.

The signals observed by proton NMR were: δ 5.4, 3.6 (t), 2.05 (s), 2.0, 1.53, 1.3-1.1, 0.9, 0.8, 0.6-0.4 ppm. The signals observed by 30 <sup>13</sup>C NMR were: δ 130, 63.2, 33.9, 32.9, 32.3, 29.6, 29.5, 25.8, 23.4, 11.7, 11.6, 11.4, 7.5, and 3.8 ppm.

The absorbances observed by FTIR were: 3322, 2951, 2873, 2853, 1457, 1414, 1377, 1341, 1235, 1168, 1057, 1014, 965, 852, 753, 721, and 586 cm<sup>-1</sup>.

5 Example 5: Synthesis of a saturated hydroxytelechelic copolymer containing *gem*-dimethyl and diethylsilane moieties

The polymer of Example 4 was hydrogenated in a Parr pressure reactor. The sample was dissolved in toluene sufficient to obtain a 10% solids solution. The hydrogenation was run at 4.14 MPa and 60°C using

10 10% Pd/C as catalyst to obtain the fully saturated hydroxytelechelic copolymer. The hydrogenation was continued until no further uptake of hydrogen was observed. The result was 58.98 g of pale yellow, fully saturated, copolymer.

The signals observed by proton NMR were: δ 3.6 (t), 1.55, 1.2, 15 0.9, 0.8, 0.5 ppm. The signals observed by <sup>13</sup>C NMR were: δ 63.1, 34.0, 32.9, 29.7, 29.4, 25.8, 24.1, 23.9, 11.8, 7.6, and 3.8 ppm.

The absorbances observed by FTIR were: 3336, 2951, 2873, 2853, 1465, 1414, 1377, 1364, 1339, 1306, 1235, 1179, 1057, 1014, 970, 755, 718, and 586 cm<sup>-1</sup>.

20 Example 6: Polyurethane synthesis using the saturated hydroxytelechelic copolymer

Inside a nitrogen-atmosphere glovebox, 5.49 g of the saturated hydroxytelechelic copolymer of Example 5, 3.61 g MDI and 59.43 g solvent (1:1 THF:dioxane containing .009 % dibutyltin dilaurate catalyst) were added to a dry 3-neck round-bottomed flask. The flask was outfitted with a heating mantle, thermocouple connected to a temperature controller, and a condenser. The solution was magnetically stirred and allowed to react at room temperature. After 2.5 hours, a sample was taken for FTIR analysis. The disappearance of the broad hydroxyl peak above 3000 cm<sup>-1</sup> showed that the diol had completely reacted with the MDI. New peaks at 3329 and 1701 cm<sup>-1</sup> confirmed the formation of urethane bonds. As expected, a large excess of isocyanate functionality remained, as indicated by a strong peak at 2275 cm<sup>-1</sup>. To

the flask, 0.89 g 1,4-butanediol (BDO) was added by syringe. The temperature of the reaction was slowly increased to 50°C. The reaction was allowed to proceed for 17 hours and was monitored by FTIR. More BDO was added in 0.04 g increments as necessary until the isocyanate peak at 2275 cm<sup>-1</sup> was very small. A total of 0.12 g more BDO was added over a period of 6 hours after the initial 17 hours of reaction time. After the last aliquot of BDO was added, the solution was held at 50°C for an additional 18 hours, at which point the isocyanate peak was extremely small.

10       The absorbances of the urethane observed by FTIR were: 3325, 3192, 3124, 3040, 2900, 2873, 2853, 2279, 1703, 1597, 1533, 1465, 1414, 1311, 1231, 1110, 1074, 1017, 962, 915, 849, 816, 769, 717, 668, 610, 586, 510 cm<sup>-1</sup>.

15       The solution was allowed to cool to room temperature and the polyurethane was precipitated into methanol in a Waring blender. The polyurethane was dried under vacuum at 70°C for 18 hours. The result was 8.99 g of white, stringy, fluffy precipitate. The polyurethane was pressed into a 0.25 mm thick film at 200°C. The film was clear with a very slight yellow tint. The film was cut into ASTM D638-5 tensile test specimens for tensile strength testing. The initial speed of the pull was 12.7 cm/minute and the crosshead speed was 12.7 cm/minute. Seven samples were tested and the results were averaged. The percent elongation at break was 146.4%. The Young's modulus was 68.4 MPa. The ultimate tensile strength was 17.6 MPa.

The complete disclosures of the patents, patent documents, and publications cited herein are incorporated by reference in their entirety as if each were individually incorporated. Various modifications and alterations to this invention will become apparent to those skilled in the art without departing from the scope and spirit of this invention. It should be understood that this invention is not intended to be unduly limited by the illustrative embodiments and examples set forth herein and that such examples and embodiments are presented by way of example only with the scope of the invention intended to be limited only by the claims set forth herein as follows.

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